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(54) Method of etching dielectric layer using a plasma generated from a mixture of flourohydrocarbon gas, NH3-genrating gas, and carbon-oxygen containing gas

(57) A method of etching a dielectric layer on a substrate with high etching selectivity, low etch rate microloading, and high etch rates is described. In the method, a substrate having a dielectric layer with resist material thereon, is placed in a process zone, a process gas is introduced into the process zone, and a plasma is formed from the process gas to etch the dielectric layer on the substrate. The process gas comprises (i) fluorohydrocarbon gas for forming fluorine-containing etchant species capable of etching the dielectric layer, (ii) NH_3-generating gas having a liquefaction temperature L_T in a range of temperatures ΔT of from about -60°C to about 20°C, and (iii) oxycarbon gas containing carbon and oxygen bonded to one another. The temperature of substrate is maintained within about ± 50°C of the liquefaction temperature L_T of the NH_3-generating gas.

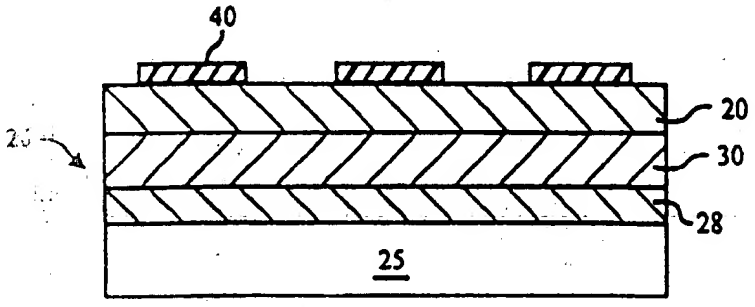

Fig. 1a

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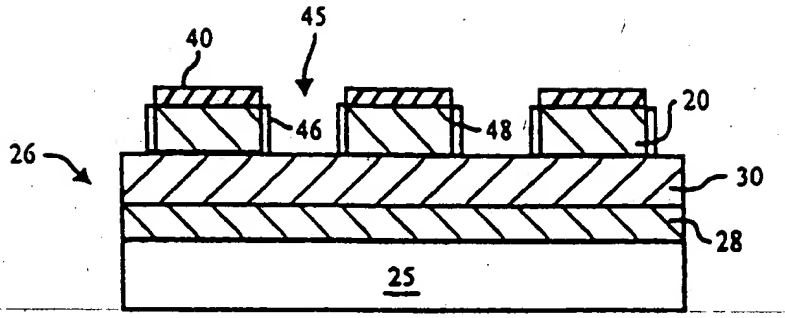

Fig. 1b

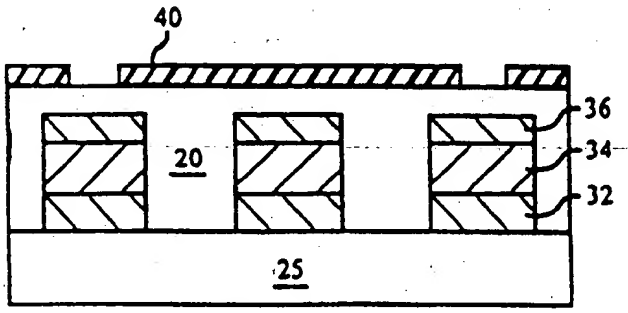

Fig. 1c

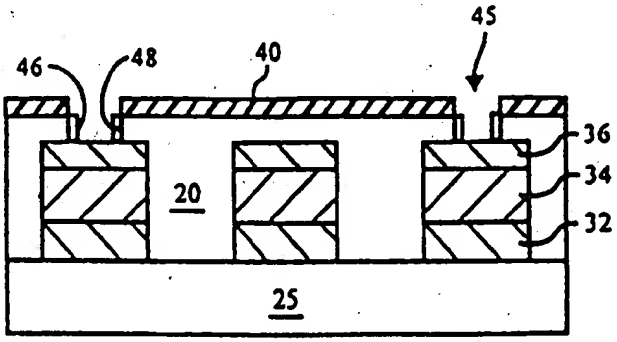

Fig. 1d

Description

The present invention relates to a process for etching substrates, and in particular, for etching dielectric layers, such as silicon dioxide, on semiconductor substrates.

In integrated circuit fabrication, it is often desirable to etch electrically insulative dielectric layers, such as silicon dioxide, undoped silicate glass, phosphosilicate glass (PSG), borophosphosilicate glass (BPSG), Si_3N_4, or TEOS deposited glass, that are used to electrically isolate devices or features formed on the substrate. For example, the dielectric layer can be deposited on a monocrystalline silicon substrate; a polysilicon layer on the substrate; or on anti-reflective or diffusion barrier layers, such as titanium silicide or titanium nitride. As another example, the dielectric layer can be deposited on electrically conductive interconnect lines that are used to electrically connect devices formed on semiconductor substrates. To etch the dielectric layer, resist material is deposited on the dielectric layer and patterned using photolithographic methods to the desired configuration of holes or lines. Holes are etched though the exposed portions of the insulative dielectric layers to the underlayers, such as silicon, polysilicon, titanium silicide, or titanium nitride layers. The etched holes are filled with electrically conductive material to form vertical electrically conductive interconnects, commonly known as contact holes or vias, which connect devices formed on the substrate or interconnect lower levels of interconnect lines to upper levels of interconnect lines.

In conventional etching processes, the dielectric layer is etched using a plasma of fluorocarbon gases, including for example, CHF_3, CH_3F, CF_4, and CH_2F_2. For example, commonly assigned U.S. patent no. 5,242,538, which is incorporated herein by reference, discloses one preferred etchant gas composition comprising CH_3F, CF_4, argon, and NH_3. The NH_3 gas is used in an amount ranging from about 5 to 20%, and more preferably about 10%, by volume of the total gas flow, to serve as a source of hydrogen radicals in the etching process. However, such conventional gas compositions do not provide dielectric etch rates exceeding 700 to 900 nm/minute, and often do not allow simultaneous control of the etch rate, etching selectivity ratio, and etch profile angle. Tailoring the gas composition to provide high etch rates results in low etching selectivity ratios and unacceptable etch profile angles, or vice versa. Modern integrated circuits often require etching selectivity ratios of greater than 10:1 with respect to the resist, and greater than 20:1 with respect to polysilicon, WSi_x, and $TiSi_x$. The etching selectivity ratio is the ratio of the dielectric etch rate to the rate of etching of the overlying resist layer, or the underlying silicon, polysilicon, titanium silicide, or titanium nitride layer. The etch profile angle, *i.e.*, the angle between the sidewall of the etched feature and the plane of the substrate, is ideally about 90° to provide features having straight and substantially perpendicular sidewalls. However, conventional etching processes often provide profile angles of less than 85°.

Another problem with many conventional etching processes is that such processes can often only be operated in a narrow processing window, *i.e.*, in a narrow range of process conditions that provide adequate etching characteristics. It is generally desirable to have a more tolerant etching process that operates in a wider range of processing conditions to allow tailoring the process conditions to achieve particular combinations of etching rates and etching selectivity ratios for different types of materials on the substrate.

It is also desirable for the etchant gas to provide dissociated carbon species that form polymeric byproduct deposits, commonly known as "passivating" layers, on the sidewalls of freshly etched features, to limit etching of the sidewalls and provide "anisotropic" etching. However, excessive deposition of passivating layers on the sidewalls of the etched features is undesirable, and can result in lower dielectric etching rates, that typically range from about 250 to 300 nm/minute.

Thus, there is a need for an etching process that provides high etching rates and good etching selectivity ratios. It is also desirable for the etching process to provide uniform profile angles of at least about 85°. It is further desirable for the etching process to operate effectively in a wide range of process conditions to allow tailoring of process conditions for particular combinations of materials.

The present invention provides a method of etching a dielectric layer supported by a silicon wafer or other substrate and having a resist layer on portions thereof, at high etch rates, with good etching selectivity, and operable in a wide range of processing conditions. The method comprises the steps of placing the substrate and the dielectric layer supported thereon in a process zone, and forming a plasma from process gas introduced into the process zone to etch the dielectric layer on the substrate. The method is characterized in that the process gas comprises (i) fluorohydrocarbon gas for forming fluorine-containing etchant species, (ii) NH_3-generating gas having a liquefaction temperature L_T from -60 to 20°C; and (iii) oxycarbon gas containing carbon and oxygen bonded to each other; and the substrate and the dielectric layer is maintained at a temperature $(L_T - 50)$°C to $(L_T + 50)$°C. It is believed that at least a portion of the NH_3-generating gas forms NH_3 chemical species that adhere to the substrate surface at the liquefaction temperatures to enhance the etching rate of the dielectric layer through surface reactions on the substrate.

The etching process provided unexpectedly high dielectric etch rates up to about 900 nm/minute in combination with excellent etching selectivity ratios. The unexpected etching properties were obtained by maintaining the volumetric flow ratio of the fluorohydrocarbon to NH_3-generating gas within a range of about 2.5:1 to about 7:1. Furthermore, wide etching processing win-

dows were obtained when carbon-oxygen gas was added. Preferably, the volumetric flow ratio of carbon-oxygen to fluorohydrocarbon gas was maintained at > 0.1:1 and ≤ 1:1.

A preferred etchant gas composition comprises (i) fluorohydrocarbon gas selected from the group consisting of CH_3F, CHF_3, C_2HF_5, and $C_2H_2F_2$, and more preferably CHF_3; and (ii) fluorocarbon gas selected from the group consisting of CF_4, C_2F_6, C_3F_8, C_4F_8, and C_4F_{10}, and more preferably CF_4. The NH_3-generating gas can comprise NH_3, NH_4OH, CH_3NH_2, $C_2H_5NH_2$, $C_3H_8NH_2$, and mixtures thereof, of which NH_3 is preferred. The carbon-oxygen gas can comprise CO, CO_2, HCOOH, $HCOHO$, CH_3COOH, CH_3OH, and mixtures thereof, of which CO is preferred. An inert gas, such as argon, capable of being activated by the plasma to sputter material from the substrate can also be added to the process gas to further enhance etch rates and provide anisotropic etching.

These and other features, aspects, and advantages of the present invention will be better understood from the following drawings, description and appended claims, which illustrate examples of the invention, where:

Figure 1a is a schematic in vertical cross-section of a dielectric layer covering a substrate;

Figure 1b is a schematic in vertical cross-section of the substrate of Figure 1a after etching of the dielectric layer showing substantially anisotropically etched contact holes;

Figure 1c is a schematic in vertical cross-section of a dielectric layer covering electrically conductive interconnection lines on a substrate;

Figure 1d is a schematic in vertical cross-section of the substrate of Figure 1c after etching of the dielectric layer showing substantially anisotropically etched vias;

Figure 2 is a schematic view in vertical cross-section of a process chamber suitable for practicing the etching process of the present invention;

Figure 3 is a graph showing the change in silicon dioxide, resist, and polysilicon etch rates as a function of the volumetric flow ratio of CHF_3 to NH_3;

Figure 4 is a graph showing the change in silicon dioxide and polysilicon etch rates for increasing flow rates of NH_3 gas;

Figure 5 is a graph showing the change in silicon dioxide and polysilicon etch rates as a function of the temperature of the support holding the substrate;

Figure 6 is a graph showing the change in profile angle for etched features as a function of the volumetric flow ratio of CHF_3 to NH_3; and

Figure 7 is a graph showing the change in silicon dioxide and polysilicon etch rates for increasing flow rates of CO gas.

The etching process of the present invention is useful for etching dielectric **20** on a substrate **25**, as shown in Figures 1a - 1d, with high etching selectivity and good etch rates. The substrate **25** can be made of any material, such as glass, ceramic, metal, polymer, or semiconductor substrates, such as a silicon or gallium arsenide wafers. The dielectric **20** on the substrate **25** typically comprises a layer of silicon oxide, phosphosilicate glass (PSG), or borophosphosilicate glass (BPSG), having thickness of about 400 to 1500 nm. The dielectric layer **20** can also comprise plurality of layers, such as for example, a silicon oxide layer having a thickness of about 100 to 500 nm, covered by a 300 to 800 nm BPSG layer. The dielectric layer **20** is used to electrically isolate devices or interconnect lines formed on the substrate **25**. For example, the dielectric layer **20** can be deposited on an underlayer **26**, such as a doped polysilicon layer **28** or a diffusion layer **30**, to electrically isolate the underlayer **26**, as shown in Figure 1a. Dielectric layers **20** are also used to cover etched interconnect lines that include (i) a lower diffusion barrier layer **32**, such as titanium, tungsten, titanium-tungsten or titanium nitride; (ii) an electrically conductive layer **34** comprising aluminum, copper and silicon; and (iii) an anti-reflective layer **36**, such as silicon, titanium nitride or titanium-tungsten, as shown in Figure 1c, each of the layers being typically from about 200 nm to about 1000 nm thick. Although the etching method of the present invention is illustrated for etching of dielectric layers, the etching method can also be used to etch films which include non-oxide layers such as silicon, polysilicon, silicide, nitride, or boride layers, for example, Ta_2O_5, TiO_2, TiN, WSi_x, and $MoSi_x$. Thus, the present invention should not be limited to etching of dielectric layers.

Typically, a photoresist **40**, such as "RISTON," manufactured by duPont de Nemours Chemical Company, is applied on the dielectric layer **20**, to a thickness of about 0.4 to about 1.3 micron, and the features **45** to be etched in the insulative dielectric layer, such as contact holes or vias, are defined using conventional lithographic processes in which the resist is exposed to a pattern of light through a mask that corresponds to the desired configuration of features **45**. The dielectric layer **20** underlying the unexposed portions of the resist are etched in the etching process. During the etching process, polymeric passivating deposits **46** are typically formed on the sidewalls **48** of the etched features **45**. The etched features **45** are typically sized from about 0.2 to about 10 microns, and more typically about 0.4 to 2 microns, and the spacing between the features is typically from

0.2 microns to 10 microns.

In the present process, the dielectric layer **20** on the substrate **25** is etched in a process chamber **50**, such as for example, an MxP OXIDE ETCH chamber, commercially available from Applied Materials Inc., Santa Clara, California, as shown in Figure 2, and generally described in commonly assigned U.S. patent nos. 4,842,683 to Cheng, et al., and 4,668,338 to Maydan, et al., both of which are incorporated herein by reference. The particular embodiment of the process chamber **50** shown herein, is suitable for processing of semiconductor substrates 25, is provided only to illustrate the invention, and should not be used to limit the scope of the invention. For example, the etching process of the present invention can be used to etch any substrate **25**, and can be used for manufacturing processes other than semiconductor fabrication.

To perform the process, the chamber **50** is evacuated to a pressure of less than about 1 mTorr, and a substrate **25** is transferred to a plasma zone **55** of the chamber **50** from a load lock transfer chamber (not shown) maintained at vacuum. Typically, the plasma zone **55** comprises a volume of at least about 5,000 cm^3, and more preferably from about 10,000 to about 50,000 cm^3. The substrate 25 is placed on a support that also serves as a cathode or anode **60**, and the sidewalls of the chamber **50** are electrically grounded to form an anode electrode **65**. The substrate **25** can be held in place during the etching process using a mechanical or electrostatic chuck (not shown) with grooves in which a coolant gas, such as helium is held to control the temperature of the substrate.

Process gas is introduced into the chamber **50** through a gas distributor 80 peripherally disposed about the substrate 25. The chamber **50** is maintained at a pressure ranging from about 1 to about 1000 mTorr, and more typically, from 10 to 300 mTorr. An electric field is maintained in the plasma zone **55** to form a plasma from the process gas (i) inductively by applying an RF current to an inductor coil (not shown) encircling the process chamber, (ii) capacitively by applying an RF current to the cathode and anode electrodes **60, 65** in the process chamber **50**, or (iii) both inductively and capacitively. In reactive ion etching (RIE) processes, the plasma is typically capacitively generated by applying an RF voltage at a power level of from about 100 to about 2000 Watts to the cathode electrode **60**, and by electrically grounding the anode electrode **65**. Alternatively, an RF current at a power level of from about 750 Watts to about 5000 Watts can be applied to an inductor coil to inductively couple energy into the chamber **50** to generate the plasma in the plasma zone **55**. The frequency of the RF current applied to the process electrodes **60, 65** or inductor coil is typically from about 50 Khz to about 60 Mhz, and more typically about 13.56 MHz.

The plasma can also be enhanced using electron cyclotron resonance or magnetically enhanced reactors, in which a magnetic field generator **85**, such as a permanent magnet or electromagnetic coils, is used to apply a magnetic field in the plasma zone **55** to increase the density and uniformity of the plasma in the plasma zone **55**. Preferably, the magnetic field comprises a rotating magnetic field with the axis of the field rotating parallel to the plane of the substrate **25**, as described in U.S. Patent No. 4,842,683, issued June 27, 1989, which is incorporated herein by reference. The magnetic field in the chamber **50** should be sufficiently strong to increase the density of the ions formed in the plasma, and sufficiently uniform to reduce charge-up damage to features **45** such as CMOS gates. Generally, the magnetic field as measured on a surface of the substrate **25** is less than about 500 Gauss, more typically from about 10 to about 100 Gauss, and most typically from about 10 Gauss to about 60 Gauss.

Spent process gas and etchant byproducts are exhausted from the process chamber **50** through an exhaust system **90** capable of achieving a minimum pressure of about 10^{-3} Torr in the process chamber. A throttle valve **95** is provided in the exhaust for controlling the pressure in the chamber **50**. Also, an optical endpoint measurement technique is typically used to determine completion of the etching process for a specific layer by measuring the change in light emission of a particular wavelength corresponding to a detectable gaseous species. A sudden decrease or increase in the amount of the detectable species, such as for example, CO or CN, that results from chemical reaction of the process gas with the silicon dioxide or polysilicon layer indicates completion of etching of the dielectric layer **20** and start of etching of the underlayer **26**.

The etching process of the present invention uses a process gas that provides high etch rates and highly selective etching of the dielectric layers **20** on the substrate **25**. The process gas includes (i) fluorohydro-carbon gas for forming fluorine-containing etchant species capable of etching the dielectric layer **20**, and for forming passivating deposits **46** on the substrate **25**, (ii) NH_3-generating gas for enhancing etching rates of the fluorine-containing etchant species by adsorping onto the surface of the substrate, (iii) carbon-oxygen gas for allowing the etching process to operate in a wider range of processing conditions, and (iv) optionally, an inert gas can be added to the process gas to provide sputtering ions that sputter material from the substrate **25**. In the etching process, the process gas is introduced into the chamber, and pressure in the chamber is maintained from about 10 to 500 mTorr, and more preferably from about 50 to about 300 mTorr. The RF power applied to the process electrodes **60, 65** is preferably from about 200 to about 2000 Watts, and more preferably from about 400 to about 1200 Watts. Preferred process gas compositions and volumetric flow ratios will now be described.

The fluorohydrocarbon gas is capable of forming fluorine-containing species that etch the dielectric layer

20 on the substrate 25. For example, a silicon dioxide layer is etched by fluorine-containing ions and neutrals, such as F, HF, F_2, CF, and CF_2 to form volatile SiF_x species that are exhausted from the chamber **50**. By fluorohydrocarbon gas it is meant a gas that includes carbon, fluorine, and hydrogen, preferred fluorohydrocarbon gases comprising, for example, CHF_3, CH_3F, C_2HF_5, CH_2F_2, and mixtures thereof. The NH_3-generating gas comprises ammonia or a gas capable of generating NH_3-containing species such as gases comprising NH_2-, NH_3, or NH_4^+ ions or molecules, including for example NH_3, NH_4OH, CH_3NH_2, $C_2H_5NH_2$, $C_3H_8NH_2$, and mixtures thereof. Of these gases, NH_3 is preferred for the reasons provided below.

It has been discovered that fluorohydrocarbon gas in combination with NH_3-generating gas provides unexpected and surprising results. Although the reaction mechanism is not fully understood it is believed that the following reaction mechanism provides increased etch rates and higher etching selectivity. The NH_3-generating gas is selected to have a high sticking coefficient on the dielectric layer 20, of preferably at least about 0.3, and more preferably at least about 0.5. The higher sticking coefficient occurs because the NH_3-generating gas has a relatively high liquefaction temperature L_T (compared to that of conventional etchant gases) of at least about -80°C, and more preferably in a range of temperatures ΔT of from about [illegible]°C to about 20°C. For example, whereas NH_3 has a liquefaction temperature of -33°C and a sticking coefficient of about 0.5; a fluorocarbon gas, such as C_2F_6, has a liquefaction temperature of about -100°C and a sticking coefficient of less than about 0.1. The higher liquefaction temperatures and higher sticking coefficients are believed to cause at least a portion of gaseous and liquid NH_3-generating phases, such as NH_3 or NH_4 species, to adsorb on the substrate 25 during the etching process and react with fluorohydrocarbon gas (for example CHF_3), on the surface of the substrate, by the following reactions:

$$2CHF_3 + NH_3 \rightarrow NH_4HF_2 + 2CF_2 \quad (1)$$

$$2CHF_3 + [illegible] \rightarrow NH_4F + HF + 2CF_2 \quad (2)$$

The chemical reactivity of the highly reactive NH_4F, HF, HF_2, and F species to the substrate surface **25** results in rapid etching of the dielectric layer **20** because the surface reactions are much faster than gas transport reactions in which relatively slow transport mechanisms limit reaction rates, including mass transport of etchant process gas species to the substrate, and etchant by-products away from the substrate.

During the etching process, the substrate **25** is cooled to temperatures sufficiently low to cause the NH_3-generating gas to adsorb onto the surface of the substrate **25**. The substrate temperatures are actually the temperatures of the support **60** used to support the substrate, which are typicaiiy 5 to 50°C lower than the true substrate temperatures and are measured by a thermocouple located within the support. Preferably, the substrate **25** is cooled to temperatures that fall in a range of temperatures within about ± 50°C, and more preferably about ± 30°C, of the liquefaction temperature L_T of the NH_3-generating gas to allow adsorbtion of the gas on the substrate surface. Thus, for liquefaction temperatures L_T within a range of temperatures ΔT of from about -60°C to about 20°C. The substrate is maintained at temperatures ranging from about -110°C to about 70°C, and more preferably from about -90°C to about 50°C. Most preferably, the substrate **25** is maintained at temperatures substantially equivalent to the liquefaction temperature L_T of the NH_3-generating gas.

One aspect of the unexpected results obtained from the present process are shown in Figure 3, which graphs etch rates obtained using a process gas comprising CHF_3 and NH_3. It is seen that the average etch rates of the dielectric, photoresist **40**, and polysilicon layers, vary nonlinearly with increasing flow ratios of CHF_3 to NH_3. The etch rate of silicon dioxide, rapidly increases at a CHF_3:NH_3 flow ratio of from 1:0 to about 2:1, as shown by the portion **202** of the curve **200**. Thereafter, the silicon dioxide etch rate rapidly decreases as the CHF_3:NH_3 flow ratio increases from about 2:1 to about 2.5:1, as shown by the portion **204**. Of particular interest is the portion **206** of the line **200**, corresponding to CHF_3:NH_3 flow ratios of from about 2.5:1 to about 7:1, where the average etch rate of the silicon dioxide layer remains relatively uniform and stable for a relatively wide range of gas flow ratios.

The average polysilicon etch rates, as shown by line **210** in Figure 3, exhibits similar behavior with the polysilicon etch rate rapidly increasing for CHF_3 to NH_3 flow ratios of 0:1 to 2:1, as shown by the portion **212** of the line **210**; and thereafter, rapidly decreasing for flow ratios of about 2:1 to about 3:1, as shown by the portion **214**. At CHF_3:NH_3 flow ratios less than about 2.5:1, the high polysilicon etch rates results in excessive etching of the polysilicon layer, and etching selectivity ratios as low as 2:1. In contrast, for CHF_3 to NH_3 flow ratios of about 2.5:1 to about 7:1, the etch rate of poiysiiicon is low and relatively stable, as shown by the portion **216**.

The resist etch rate, as shown by the line **220** of Figure 3, initially rapidly decreases for CHF_3:NH_3 flow ratios between 0:1 to 3:1, as shown by the portion **222**, and thereafter, more gradually decreases to zero, as shown by the portion **226**. Operation of the etching process in the portion **222**, at low CHF_3:NH_3 flow ratios of less than 2.5:1, would provide narrow processing windows because the dielectric etch rates changes rapidly for small changes in process gas flow rates, and normal flow rate fluctuations would cause significant variability in etch rates between different process runs. Also, the high resist etching rates at these flow ratios can result

in resist faceting and etching of the dielectric layer **20** below the resist.

Figure 3 demonstrates that a fluorohydrocarbon to NH_3-generating gas flow ratios of from about 2.5:1 to about 7:1, and more preferably from 3:1 to 6:1, provides stable and high etch rates of at least about 400-500 nm/minute, while simultaneously providing good etching selectivity ratios for etching of silicon dioxide relative to resist and polysilicon. These flow ratios correspond to the portion 206 of the SiO_2 etch rate line **200**, the portion **216** of the polysilicon etch rate line **210**, and the portion **222** of the resist etch rate line **220**. In these portions of the etching rate curves, the low polysilicon and resist etch rates provide high etching selectivity ratios; while simultaneously the dielectric etch rates are maintained at relatively high levels. Also, the dielectric polysilicon and resist etching rates remain relatively stable and uniform over a wide range of gas flow ratios to provide a wide processing window. These unexpected results demonstrate the importance of using a CHF_3 and NH_3 combination in the specified volumetric flow ratios to provide optimal etching rates and etching selectivity ratios.

With reference to Figures 4 and 5, it is seen that the dielectric etch rates vary non-linearly as a function of the flow rate of the NH_3-generating gas, and the temperature of the support holding the substrate (commonly referred to as substrate temperature). Fiyure 4 shows that the average SiO_2 dielectric etch rates vary in the form of an upside down U-shaped curve, with dielectric etch rates increasing as NH_3 flow rates from 0 to 25 sccm, and decreasing as NH_3 flow rates from 25 to 50 sccm. Similarly, the polysilicon etch rates also peak at an NH_3 flow rate of about 25 sccm, although to a lesser degree. The unusual U-shaped variation in etch rates for increasing flow of NH_3 is not anticipated from the prior art, and demonstrates the unexpected results of the present invention.

Figure 5 shows the change in average dielectric and polysilicon etch rates as a function of increasing substrate temperature. It is seen that while the etch rate of the SiO_2 dielectric layer decreases with increasing temperature, the etch rate of the polysilicon layer, which affects the etch selectivity ratio, does not significantly change with increasing temperatures. This graph demonstrates that increasing substrate temperature significantly decreases etching rates, and higher substrate temperatures are needed to slow down the rate of etching of the dielectric layer **20** during etching of thin dielectric layers, such as BPSG or silicon dioxide layers. Also, a relatively wide temperature range can be used without significantly affecting selectivity ratios, which does not significantly change with increasing temperatures.

Furthermore, the unusual etching characteristics of the carbon and NH_3-generating gas mixture, such as the change in profile angle of etched features 45 with increasing flow ratio of fluorohydrocarbon to NH_3-generating gas, as shown in Figure 6. The profile angle of the etched features were measured using the average value of multiple measurements of etched contact holes having diameter of about 0.8 µm, at both the center and edge of the wafer, using SEM (Scanning Electron Microscope) photographs of cross-sections of the etched substrate **25**. It was observed that at low flow ratios of CHF_3:NH_3, namely at flow ratios less than about 2.5:1, the profile angles of the etched features **45** are typically less than 80°, and often as low as 70°. Furthermore, CHF_3:NH_3 flow ratios higher than 5:1 also provided low profile angles of less than about 75°. In contrast, CHF_3:NH_3 volumetric flow ratios ranging from 2.5:1 to 5:1 provided optimal profile angles typicaiiy ranging from about 80° to about 90°, arid more typically from about 85° to 90°.

For these reasons, the volumetric flow ratio of fluorohydrocarbon to NH_3-generating gas is selected specifically for particular material combinations to provide (i) a dielectric etch rate of at least about 500 nm/minute, (ii) a dielectric to resist etching selectivity ratio of at least about 10:1, and more typically at from 100:1 to ∞:1, and (iii) a dielectric to underlayer etching selectivity ratio of at least about 25:1. The volumetric flow ratio of fluorohydrocarbon to NH_3-generating gas can also be adjusted so that the etched features **45** have profile angles of at least about 85°. As described above, preferred volumetric flow ratios of fluorohydrocarbon to NH_3-generating gas that provide high etch rates, good etching selectivity, and excellent profile angles, are from about 2.5:1 to about 7:1, and more preferably are from 3:1 to about 6:1. Although, preferred ranges of volumetric flow ratios are described herein, it should be understood that the volumetric flow ratios can be tailored for different combinations of materials, and to achieve specific etching selectivities, etch rates, or etched feature geometries, for example aspect ratios or profile angles, without deviating from the scope of the present invention.

It is further discovered that the addition of oxycarbon gas or carbon-oxygen gas (by which it is meant a gas containing carbon and oxygen bonded to each other) to the process gas allows the etching process to operate in a wider range of processing conditions, such as process gas flow rates, pressures, temperatures, and RF power levels. Preferred oxycarbon or carbon-oxygen gases include CO, CO_2, HCOOH, HCOHO, CH_3COOH, and CH_3OH. The oxycarbon or carbon-oxygen gas typically reacts with fluorine-containing species to form volatile COF_2, thereby reducing the fluorine concentration in the process chamber **50** and consequently reducing the rate of etching of polysilicon to provide higher etching selectivity ratios. In addition, the carbon-oxygen gas enhances the formation of free carbon and CF_2 species that react with other species, such as nitrogen, fluorine, and boron to form polymeric passivating deposits **46** on the sidewalls of the etched features **45** to provide anisotropic etching of the dielectric layer. However, excessively high flow rates of the carbon-oxygen gas can cause thick passivating deposits **46** to

form on the substrate resulting in lower dielectric etch rates. The flow rate of carbon-oxygen gas is maintained less than, or substantially equal to, the flow rate of the fluorohydrocarbon gas to provide sufficient fluorine-containing species to rapidly etch the substrate while providing high etching selectivity and anisotropic etching. Preferably, the volumetric flow ratio of the carbon-oxygen gas to fluorohydrocarbon gas is at least about 1:1 and less than or equal to about 1:1.

The addition of carbon-oxygen gas to the process gas substantially increases the processing window of the etching process to be operated in a wider range of conditions. With reference to Figure 7, increasing flow rates of the carbon-oxygen gas provide a substantial reduction of the polysilicon etch rate from about 5 nm/minute to almost 0 nm/minute while simultaneously maintaining the silicon dioxide etch rate substantially constant at about 650 nm/minute. The addition of carbon-oxygen gas significantly increases the etching selectivity ratio of silicon dioxide to polysilicon while maintaining high and controllable silicon dioxide etch rates. This allows tailoring the gas composition by increasing the flow rate to achieve desired etching characteristics providing high dielectric etch rates over a wide range of process conditions.

Preferably, argon is added to the process gas to provide efficient etching through highly directional bombardment of the substrate **25** by charged inert gas ions energized by the electric field in the chamber. Argon gas also assists in sputtering-off the deposits **46** on the sidewalls of the features **45** to reduce the thickness of such deposits. It is desirable for the inert gas to have high ionization energies, so that the inert gas forms ionized metastable states that promote dissociative reactions which promote etching reactions. Suitable inert gases include argon, neon, and krypton, of which argon is preferred. The inert gas is added to the process gas to provide desired anisotropic etching characteristics and dissociation of the process gas. However, excessive argon flow rates can cause excessive ion bombardment on the substrate **25**, resulting in undesirable sputtering of the dielectric layer **20** underlying the features. The charged argon ions also enhance the dissociation of the NH_3 or NH_4 species adsorbed on the substrate **25** by ion bombardment to provide anisotropic etching characteristics. Preferably, the volumetric flow ratio of inert gas to carbon-oxygen gas is from about 0.1:1 to about 10:1, and more preferably from about 1:1 to about 3:1.

In the present invention, the process gas composition of (i) fluorohydrocarbon gas and (ii) carbon-oxygen gas that are absent hydrogen, such as C_3F_8, C_4F_8 and C_4F_{10}. It has been found that the combination of the fluorohydrocarbon and fluorocarbon gases provides optimum etch rates and etching selectivity ratios. Although the gas chemistry is not fully understood, it is believed that the fluorohydrocarbon gas provides hydrogen species that combine with free fluorine radicals to form gaseous HF that is exhausted from the chamber **50** to increase the carbon available to form passivating deposits **46**, and limiting the fluorine species available for etching the dielectric **20**. In contrast, the fluorocarbon gas provides increased amounts of free fluorine that balances microloading effects. However, excessive amounts of fluorohydrocarbon gas provides etched features having tapered or sloped sidewalls because of the high carbon content that results in increased passivating deposits on the sidewalls of the features. A preferred combination of gases include a fluorocarbon such as CF_4, and a fluorohydrocarbon such as CHF_3, in a volumetric flow ratio of about 0:1 to about 1:2, and more preferably from about 0.1:1 to about 1:20.

One preferred composition of process gas suitable for etching silicon dioxide layers on a silicon substrate **25** with high selectivity, comprises CHF_3, NH_3, CO, CF_4, and argon. For the volume within the process chamber **50** described herein, (i) a suitable flow rate of fluorohydrocarbon gas, such as CHF_3, is from about 5 to about 200 sccm, and more preferably from 10 to 100 sccm; (ii) a suitable flow rate of NH_3-generating gas is from about 2 to about 50 sccm, and more preferably from about 4 to about 20 sccm; (iii) a suitable flow rate of CO is from about 0 to about 200 sccm, and more preferably from about 10 to about 100 sccm; (iv) a suitable flow rate of fluorocarbon gas, such as CF_4, is preferably from about 0 to about 40 sccm, and more preferably from about 2 to about 20 sccm; and (v) a suitable flow rate of inert gas, such as argon, is from about 5 to about 300 sccm, and more preferably from about 15 to about 200 sccm. Because flow rates are selected depending upon the volume of the chamber **50**, the invention should not be limited to the flow rates recited herein.

EXAMPLES

The following illustrative examples of the present invention are shown to etch dielectric layers **20** on semiconductor substrates **25**, with high etch rates, and high etching selectivity ratios. However, the apparatus and method of the present invention can be used in other applications as would be apparent to those skilled in the art, and the scope of the present invention should not be limited to the illustrative examples provided herein.

In these example, the substrates **25** comprised silicon wafers having a diameter of 200 mm (8 inch), and coated with different layers, such as polysilicon, conductivity enhancement layers, or diffusion barrier layers **32**, as described below. In each experiment the substrate **25** was placed on the cathode **60** of an MxP OXIDE ETCH chamber **50**, the chamber **50** was maintained at a pressure of from about 80 mTorr to about 250 mTorr.

Process ... CHF_3 and NH_3 was used. The substr... temperatures ranging within about ... action temperature L_T of NH_3 gas wh... using a flow of helium on the backsid... 25 maintained at a pressure of abou... was generated in the plasma zone 55 ... voltage to the process electrodes ... vel of about 1000 Watts. The plasma ... applying a rotating magnetic field of ... the plasma zone **55**.

Sc... ic optical microscopy techniques ... sure the (i) etch rates of the dielect... layers, and (ii) etch rate uniformity ... culated by measuring the depth ... ched in the wafers. The etching sel... culated from the ratio of the etch ra... ayers **20** to the etch rate of the TiS... st layers.

Exam...

Th... (... d to demonstrate use of a proces... ohydrocarbon gas, NH_3-gener... gas, and inert gas. In this exam... 20 on the substrate **25** comprised ... having a thickness of 1 to 2 µm, ... on underlayer **26** having a thickn... The dielectric layer **20** was etche... ter contact holes.

A... ing 40 sccm CHF_3, 11 sccm NH_3, ... cm Ar was used. This gas comp... $_3$ flow ratio of about 4:1. The p... 0 was maintained at 138 mTorr... ined at a temperature of -30°C ... rom the process gas by applyi... evel of about 1000 Watts to the ... process chamber **50**, and the pl... sing a rotating magnetic field h... Gauss.

E... the effectiveness of a CHF_3... 1:1, which provided a silicon ... g 600 nm/minute. In addition, ... for etching silicon dioxide re... 00:1 were obtained, and etchi... on dioxide to photoresist of ∞:1 ... so, etched profile angles greate... d.

Exam...

T... to demonstrate the effect of a ... rohydrocarbon gas:NH_3-gener... trate use of fluorocarbon gas. I... ctric layer **20** comprised boron ... (BPSG) having a thickness ... underlayer **26** comprising Ti... A.

T... sed 55 sccm CHF_3, 11 sccm NH_3, 11 sccm CF_4, and 80 sccm Ar. This gas composition had a CHF_3:NH_3 ratio of about 5:1. The pressure in the chamber **50** was maintained at 225 mTorr, and the support maintained at a temperature of -30°C. A plasma was formed from a process gas for applying a current at a power level of about 1000 Watts to the electrodes **60, 65** in the process chamber **50**, and the plasma was enhanced using a rotating magnetic field having a strength of 38 Gauss.

Example 2 demonstrated the effectiveness of a CHF_3:NH_3 ratio of about 5:1 for etching of contact holes having a diameter of 0.4 µm in a BPSG layer. BPSG etching rates greater than 900 nm/minute were obtained, and the etching selectivity ratio of BPSG to TiS_2 was greater than 25:1. The etching process also provided average profile angles of greater than 86°.

Example 3

This example is provided to demonstrate the effect of a different flow ratio of fluorohydrocarbon gas:NH_3-generating gas, in a process gas comprising fluorocarbon gas. In this example, the substrate **25** comprised a dielectric layer **20** of silicon oxide in a thickness of 1.6 µm deposited on a titanium nitride layer having a thickness of 500 Å. Via holes having a diameter of about 0.4 µm were etched in the dielectric layer **20**.

A process gas comprising 33 sccm CHF_3, 11 sccm NH_3, 5 sccm CF_4, and 66 sccm Ar, was used. This gas composition provided a CHF_3:NH_3 flow ratio of about 3:1, and a CHF_3:CF_4 flow ratio of about 6.6:1. The pressure in the chamber **50** was maintained at 138 mTorr, and the support maintained at a temperature of -30°C. A plasma was formed from a process gas by applying a current at a power level of about 1000 Watts to the electrodes **60, 65** in the process chamber **50**, and the plasma was enhanced using a rotating magnetic field having a strength of 38 Gauss.

In example 3, the silicon dioxide dielectric layer was etched at etch rates greater than 900 nm/minute, and an etching selectivity ratio of silicon dioxide to TiN of greater than 30:1 was obtained. The etched features **45** had a profile angle of greater than 89°.

Example 4

This example is provided to demonstrate use of a process gas comprising fluorohydrocarbon gas, NH_3-generating gas, carbon-oxygen gas, fluorocarbon gas, and inert gas, to show the advantages of adding carbon-oxygen gas to the process gas.

The process gas comprised 40 sccm CHF_3, 11 sccm NH_3, 40 sccm CO, 11 sccm CF_4, and 80 sccm Ar. This gas composition provided a CHF_3:NH_3 ratio of about 4:1, and a CO:CHF_3 ratio of about 1:1. The pressure in the chamber **50** was maintained at 138 mTorr, and the support maintained at a temperature of -30°C. A plasma was formed from a process gas by applying a

current ...bout 1000 Watts to the electrodes ... chamber **50**, and the plasma wa... ...ating magnetic field having a stren...

Th... ...d an etching selectivity ratio of etch... ...olysilicon of ∞:1, which is a signific... ...er conventional processes. In add... ...h rates of greater than 600 nm/mi... ...The extremely high polysilicon et... ...n combination with high silicon d... ...ovides a large process window fo... ...trate **25** in a range of different pr... ...out significantly reducing the etching... ...oxide layer. This is a particularly ... ...ing the gas composition for highly ... ...different material combinations ...

Th... ...s to an etching process that uses ... ...and process conditions to obtain ... ...s of up to 900 nm/minute (9000 ... ...electivity ratios exceeding 100:1, ...:1; and etching profile angles h... ...been discovered that the combi... ...carbon and NH_3-generating gas ... ...NH_3, provide excellent dielectri... ...acrificing the etching selectivity ... ...con. It has further been discovered ... ...and polysilicon etch rates chang... ...d curve for increasing flow ratios ... ...NH_3-generating gas, and at pre... ...ng from about 2.5:1 to 7:1 provid... ...tric etch rates and etching selec... ...n of carbon-oxygen gas to the flu... ...H_3-generating process gas provid... ...dows, by providing high dielectr... ...e of processing conditions, witho... ...tivity ratios. The unusual adva... ...is combination of process gas is ... ...d by the prior art, and results i... ...nts in the field of etching dielec...

A ...ention has been described in co... ...gard to the preferred versions ... ...are possible. For example, gase... ...r composition to the fluorohyd... ...rating gas, or carbon-oxygen g... ...d the etching process can be us... ...rials, such as for example silicid... ...d carbides. Therefore, the appe... ...e limited to the description of the ...ained herein.

Claim...

1. A ...electric layer supported by a ...bstrate, the method comp... ...ng the substrate and the dielectric layer supported thereon in a process zone, and forming a plasma from process gas introduced into the process zone to etch the dielectric layer on the substrate;

characterized in that:

(1) the process gas comprises (i) fluorohydrocarbon gas for forming fluorine-containing etchant species, (ii) NH_3-generating gas having a liquefaction temperature L_T from -60 to 20°C; and (iii) oxycarbon gas containing carbon and oxygen bonded to each other; and
(2) the substrate and the dielectric layer is maintained at a temperature (L_T- 50)°C to (L_T+ 50)°C.

2. A method according to claim 1 characterized in that

(1) the NH_3-generating gas is one or more of NH_3, NH_4OH, CH_3NH_2, $C_2H_5NH_2$, and $C_3H_8NH_2$;
(2) the fluorohydrocarbon gas is one or more of CHF_3, CH_3F, C_2HF_5, and $C_2H_2F_2$; and
(3) the oxycarbon gas is one or more of CO, CO_2, HCOOH, CH_3COOH, and CH_3OH.

3. A method according to claims 1 or 2 characterized in that the volumetric flow ratio of:

(1) fluorohydrocarbon gas to NH_3-generating gas is from 2.5:1 to 7:1; and
(2) oxycarbon gas to fluorohydrocarbon gas is from 0.1 to 1:1.

4. A method according to any one of the preceding claims characterized in that the process gas further comprises a fluorocarbon gas which is one or more of CF_4, C_2F_6, C_3F_8, C_4F_8, and C_4F_{10}.

5. A method according to claim 4 characterized in that the fluorohydrocarbon gas is CHF_3, the fluorocarbon gas is CF_4, and the volumetric flow ratio of CF_4 to CHF_3 is less than about 1:2.

6. A method according to any one of the preceding claims characterized in that the process gas further comprises an inert gas which is one or more of argon, xenon, neon, krypton, or helium; and the volumetric flow ratio of inert gas to fluorohydrocarbon gas is from 1:1 to 3:1.

7. A method of etching a dielectric layer supported by a silicon wafer or other substrate, the method comprising the steps of placing the substrate and the dielectric layer supported thereon in a process zone, and forming a plasma from process gas introduced into the process zone to etch the dielectric layer on the substrate;

...terized in that the process gas is a mixture of BF_3, F_4, NH_3, CO, and inert gas.

8. A ... according to claim 7 characterized in that th... strate and dielectric layer thereon is maintained at temperatures from -110°C to 70°C.

9. A ... according to claim 7 or 8 characterized in that ... metric flow ratio of

(... F_3 to NH_3 is from 2.5:1 to 7:1;
... O to CHF_3 is from 0.1:1 to 1:1; and
... F_3 to CHF_3 is from 0:1 to 1:2.

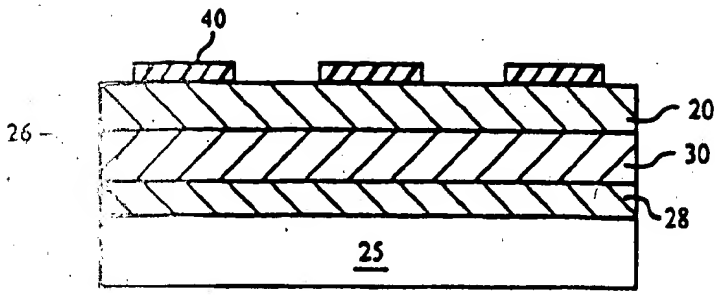

Fig. 1a

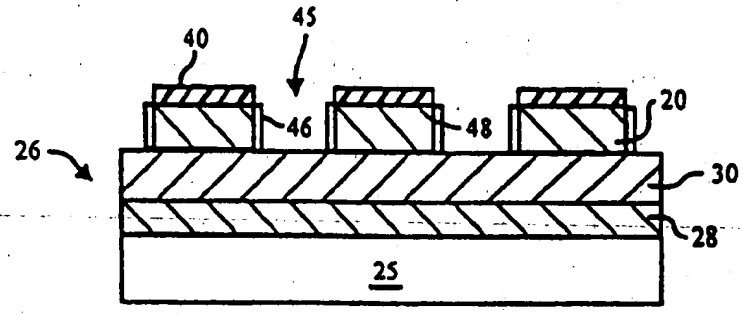

Fig. 1b

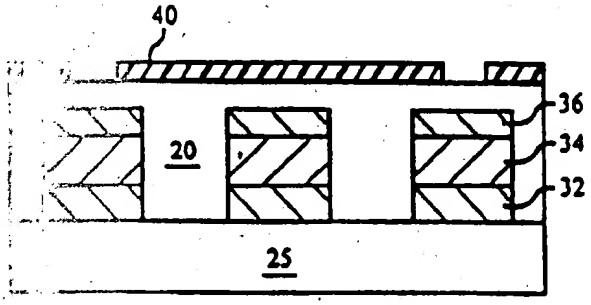

Fig. 1c

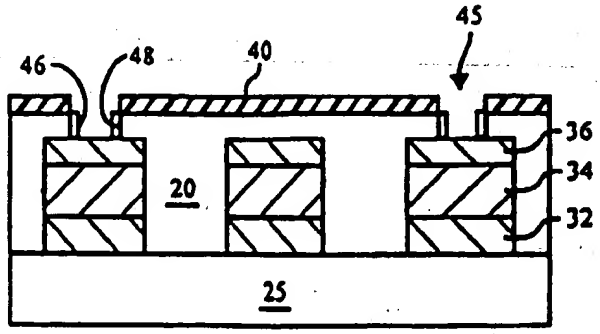

Fig. 1d

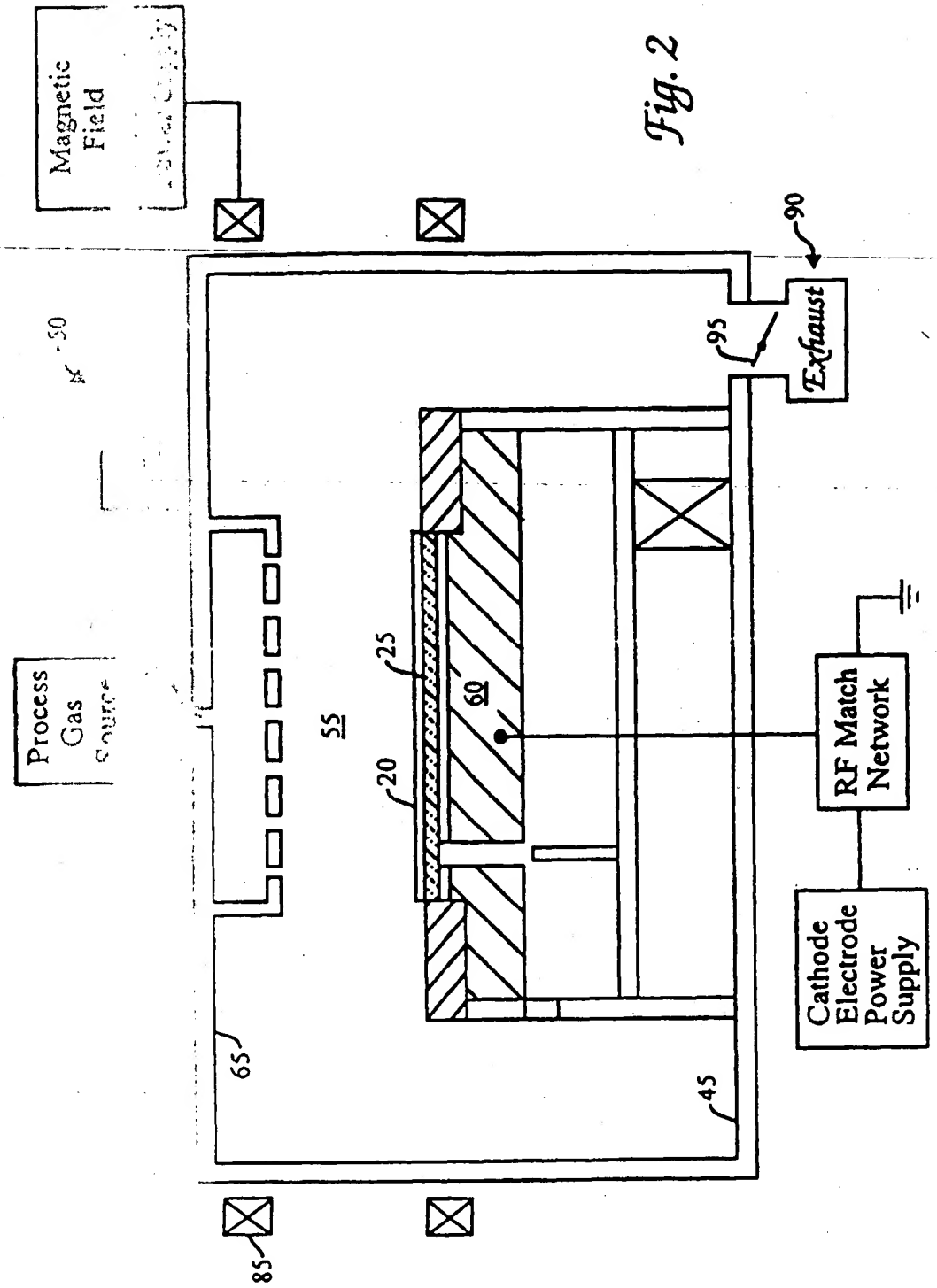
Magnetic Field
Power Supply
50
90
Exhaust
95
Process Gas Source
55
25
60
20
RF Match Network
Cathode Electrode Power Supply
65
45
85

Fig. 2

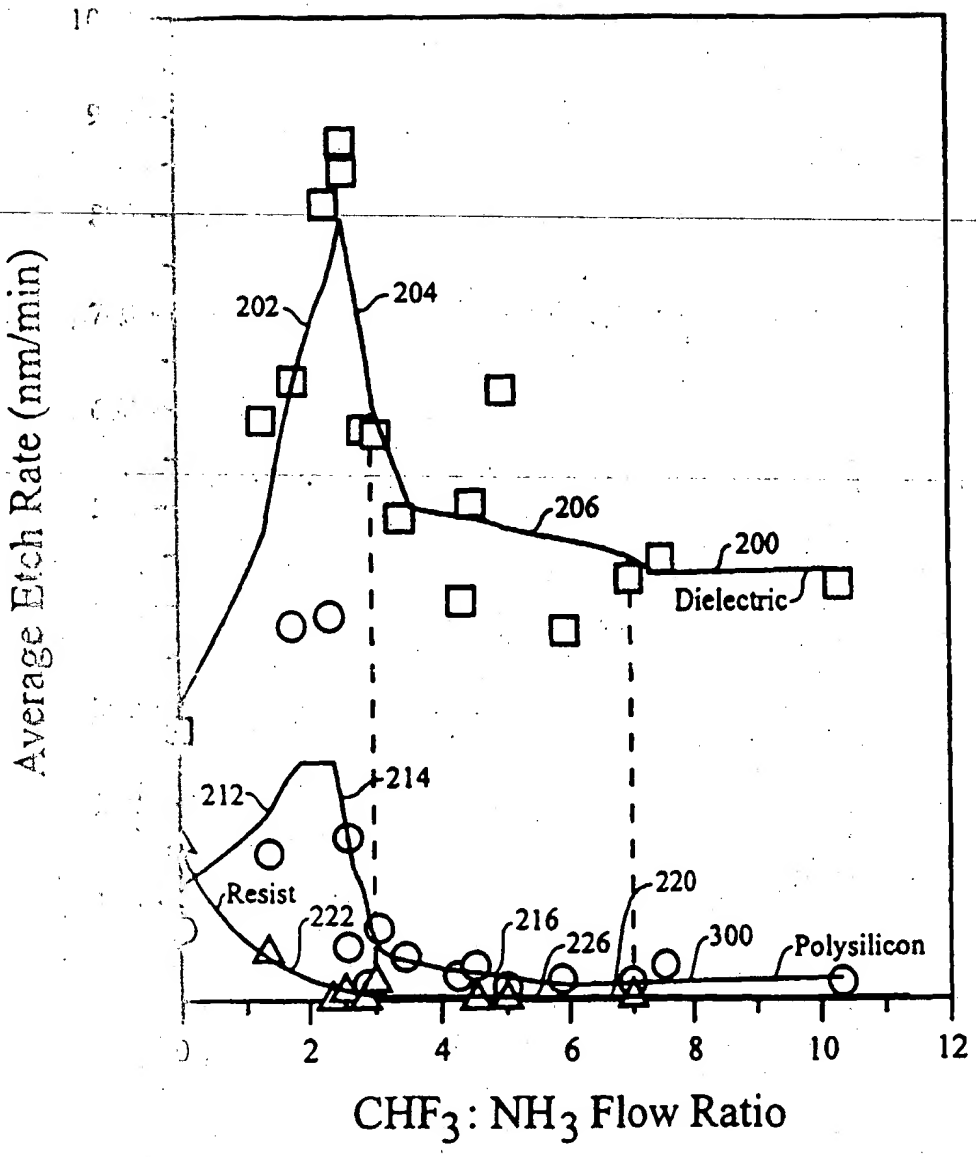
Average Etch Rate (nm/min)
202
204
206
200
Dielectric
212
214
Resist
222
216
226
220
300
Polysilicon
0
2
4
6
8
10
12
$CHF_3 : NH_3$ Flow Ratio

Fig. 3

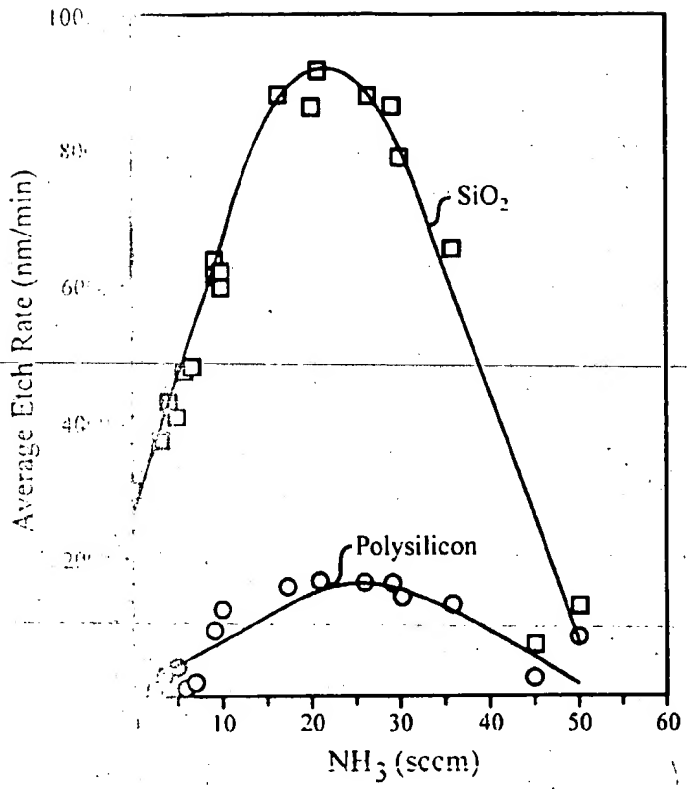

Fig. 4

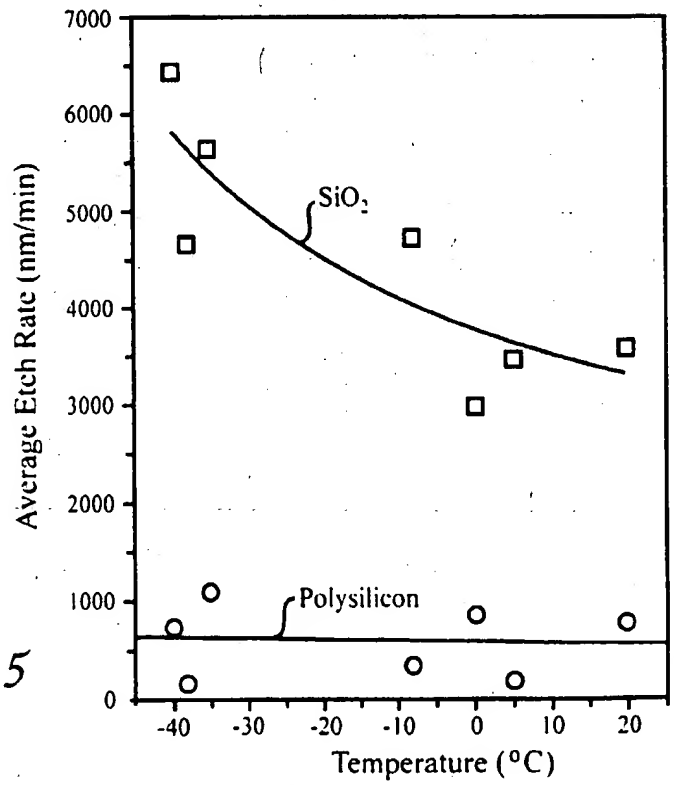

Fig. 5

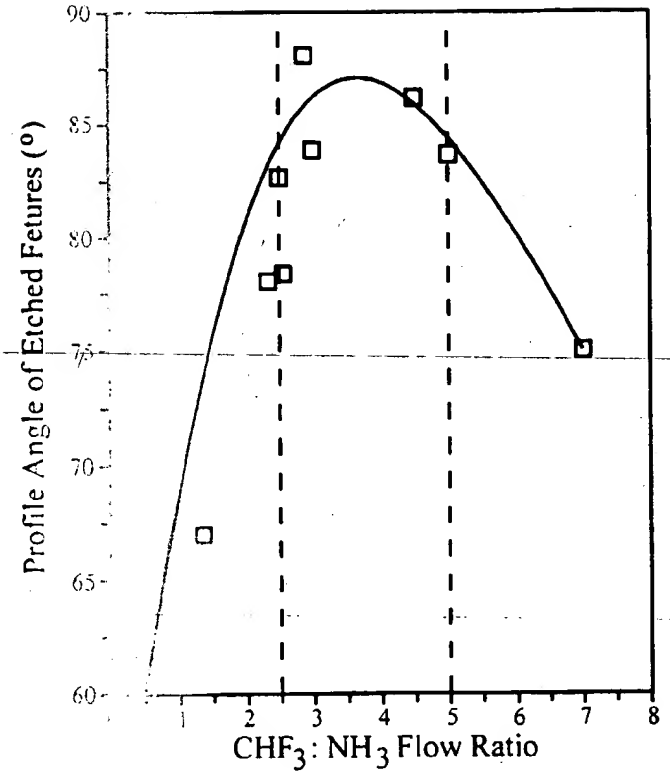

Fig. 6

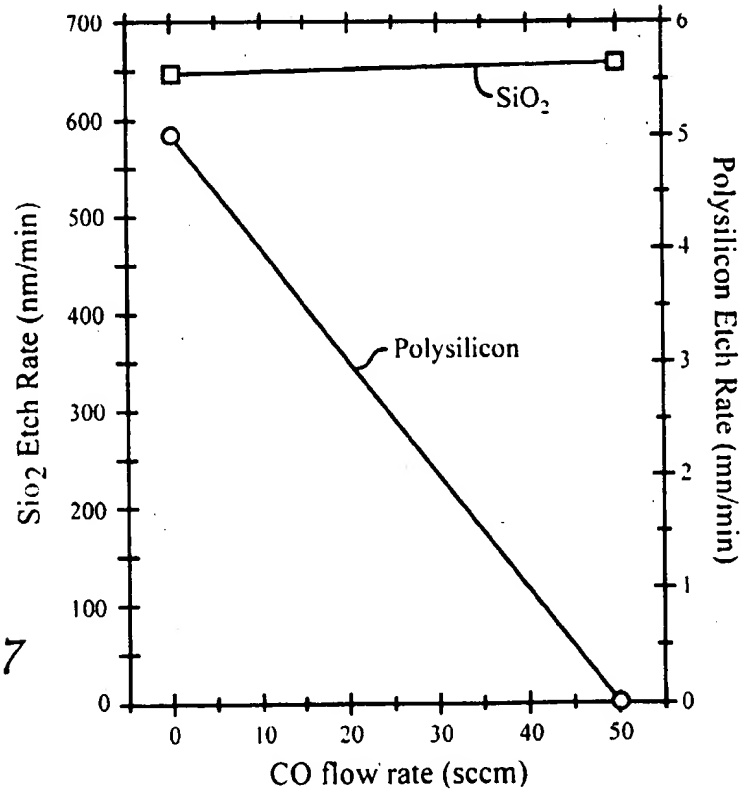

Fig. 7

DERWENT-ACC-NO: 1998-035216
DERWENT-WEEK: 199846
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TITLE: Etching dielectric layers at high etch rates, high selectivity ratios etc. - using plasma formed from mixture of fluoro-hydrocarbon, ammonia-generating, oxycarbon and optionally fluorocarbon and inert gases

INVENTOR: DING, C; SHAN, H ; WELCH, M ; DING, J

PATENT-ASSIGNEE: APPLIED MATERIALS INC[MATEN]

PRIORITY-DATA: 1996US-0660966 (June 12, 1996) , 1996US-0639388 (April 29, 1996)

PATENT-FAMILY:

PUB-NO	PUB-DATE	LANGUAGE	PAGES	MAIN-IPC
EP 813233 A2	December 17, 1997	E	016	H01L 021/311
JP 10056001 A	February 24, 1998	N/A	012	H01L 021/3065
US 5814563 A	September 29, 1998	N/A	000	H01L 021/302

DESIGNATED-STATES: AT BE CH DE DK ES FI FR GB GR IE IT LI LU MC NL PT SE

CITED-DOCUMENTS: No-SR.Pub

APPLICATION-DATA:

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EP 813233A2		1997EP-0304035	June 10, 1997
JP10056001A		1997JP-0147995	June 5, 1997
US 5814563 A	Cont of	1996US-0639388	April 29, 1996
US 5814563A		1996US-0660966	June 12, 1996

INT-CL_(IPC): H01L021/302; H01L021/3065 ; H01L021/311 ; H01L021/768

RELATED-ACC-NO: 1997-538384

ABSTRACTED-PUB-NO: EP 813233A

BASIC-ABSTRACT: A method of etching a dielectric layer supported by a silicon wafer or other substrate comprises: (a) placing the substrate supporting the dielectric layer in a process zone; (b) etching the dielectric layer using a plasma formed from a process gas comprising (i) fluoro-hydro carbon gas for forming fluorine containing etchant species; (ii) ammonia-generating gas having a liquefaction temperature LT of -60 to 20 deg. C; and (iii) oxycarbon gas; and (c) the substrate and dielectric layer are maintained at (LT-50) deg. C to (LT+50) deg. C.

USE - In addition to silicon oxide, the process can be used to etch, e.g. silicides, nitrides, and carbides. The process is useful in semiconductor integrated circuit fabrication to electrically isolate devices or features formed on a substrate (e.g. monocrystalline silicon, polysilicon layers, anti-reflective or diffusion barrier layers, e.g. titanium silicide or titanium nitride); and etching holes between interconnect lines, the holes

being subse[illegible]ntly filled with electrically conductive material to form vertical inte[illegible] (holes or vias) to connect devices formed on the substrate or [illegible]nnect lower levels of interconnect lines to upper levels of interconn[illegible]

ADVANTAGE [illegible]gh etching selectivity ratios of etching silicon oxide to polysilicon, e[illegible] > 100:1, etching profile angles higher than 85 deg. , and silicon oxide [illegible] rates of 600-900 nm/minute (9000 Angstrom /minute), providing lar[illegible]ocessing windows under a range of different process conditions.

ABSTRACTED-PUB-NO: US 5814563A

EQUIVALENTS: A method of etching a dielectric layer supported by a silicon wafer [illegible] substrate comprises: (a) placing the substrate supporting t[illegible]electric layer in a process zone; (b) etching the dielectric layer using a [illegible]ma formed from a process gas comprising (i) fluoro-hydro carbon gas f[illegible]ng fluorine-containing etchant species; (ii) ammonia-ge[illegible]gas having a liquefaction temperature LT of -60 to 20 deg. C; and (iii) ox[illegible]gas; and (c) the substrate and dielectric layer are maintained a[illegible]deg. C to (LT+50) deg. C.

USE - In addi[illegible]silicon oxide, the process can be used to etch, e.g. silicides, bo[illegible]ni[illegible]des, and carbides. The process is useful in semiconduc[illegible]ated circuit fabrication to electrically isolate devices or features forr[illegible] substrate (e.g. monocrystalline silicon, polysilicon layers, anti-r[illegible]or diffusion barrier layers, e.g. titanium silicide or titanium nitri[illegible] etching holes between interconnect lines, the holes being subse[illegible]ed with electrically conductive material to form vertical inter[illegible]c[illegible] (holes or vias) to connect devices formed on the substrate or [illegible]nnect lower levels of interconnect lines to upper levels of interconn[illegible]

ADVANTAGE [illegible]ching selectivity ratios of etching silicon oxide to polysilicon, [illegible]1, etching profile angles higher than 85 deg. , and silicon oxide [illegible]s of 600-900 nm/minute (9000 Angstrom /minute), providing lar[illegible]sing windows under a range of different process conditions.

CHOSEN-DR[illegible]wg.0/7

TITLE-TERM[illegible]

ETCH DIELE[illegible]YER HIGH ETCH RATE HIGH SELECT RATIO PLASMA FORMING MIXTURE FLUORO HY[illegible]ON AMMONIA GENERATE OXY CARBON OPTION FLUOROCARBON INERT GAS

ADDL-INDEX:[illegible]MS:

INTERCONN[illegible]E VIAS SILICIDE BORIDE NITRIDE CARBIDE

DERWENT-C[illegible]3 U11

CPI-CODES:[illegible];

EPI-CODES:[illegible]3; U11-C07A1; U11-C07C3; U11-C08A5;

UNLINKED-D[illegible]-REGISTRY-NUMBERS: 0246U; 0247U ; 0270U ; 0330U ; 0341U ; 0367U

; 0378U ; 0814 U ; 1403U ; 1423U ; 1534U ; 1671U ; 1713U

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CPI Secondar sion Numbers: C1998-011949
Non-CPI Seco ccession Numbers: N1998-028283